Comment on "Electron Correlation Effects in Resonant Inelastic X-ray Scattering of NaV_2O_5"

Recently, Zhang *et al.*[1] studied the Resonant Inelastic X-ray Scattering (RIXS) of the ladder compound NaV_2O_5. This work clearly demonstrates the ability of RIXS to study the valence properties of strongly correlated systems. In their interpretation, the absorption process puts an electron in the upper Hubbard band and the radiative decay creates a hole in the lower Hubbard band, resulting in an excitation across the Hubbard gap with an energy proportional to U. However, this description is based on some assumptions that are not justified.

First, it is unlikely that the gap in NaV_2O_5 is proportional to U. *Ab initio* calculations[2] show that the d_{xy} orbitals of a V-O-V rung form bonding and antibonding molecular orbital states as a result of $t_\perp \cong 0.38$ eV. Dispersion of these states is caused by hopping along the ladder, $t_{||} \cong 0.17$ eV. Within an independent-particle framework, the ground state would be a half-filled band consisting bonding d_{xy} molecular orbitals. Insulating behavior follows from an on-site Coulomb interaction U of 2-5 eV. Since $U \gg t_\perp$, a strong coupling picture is necessary. The charge-transfer gap is then not proportional to U but of the order $2t_\perp - J_\perp$, where $J_\perp \cong 4t_\perp^2/U$.

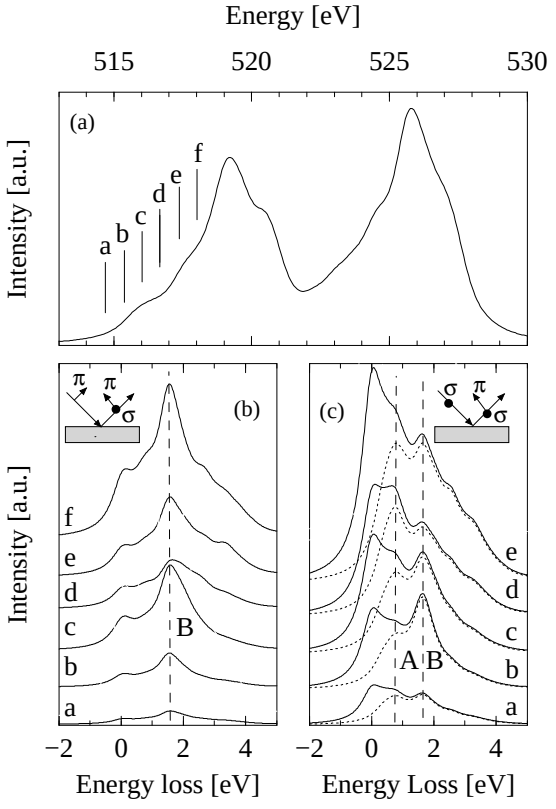

FIG. 1: (a) The solid line shows the XAS spectrum for a four-site cluster. The letters $a - f$ indicate the various incident energies. RIXS data on an energy-loss scale in the $\pi \rightarrow \pi\sigma$ and $\sigma \rightarrow \pi\sigma$ configurations are shown in (b) and (c), respectively. Also shown in (c) are the RIXS spectra with the elastic contribution removed (dotted line).

Secondly, RIXS at the L-edge in transition metal compounds is not well suited to study charge-transfer excitations. Since dipolar transitions into the $3d$ shell are made, the core hole potential is directly screened by the excited electron and mainly local transitions are made. This is in contrast with RIXS at the K edge, where a charge transfer between rungs is needed to screen the core hole.

Thirdly, the polarization condition used in the experiment does not allow the observation of the lowest excited state of NaV_2O_5. Figure 1(b) and (c) show the RIXS spectra for the aborption energies indicated by labels a-f in Fig. 1(a) for two different polarization conditions (see insets). Calculations were done for a four site Hubbard model of d_{xy} orbitals. On the site where the RIXS process takes place all the $2p$ and $3d$ orbitals are taken into account and spin-orbit coupling and the full dd and pd multiplet interaction are included. The spectra are given on an energy loss scale, $\omega - \omega'$. The RIXS spectra in the paper by Zhang *et al.* [1] were measured in a $\pi \rightarrow \pi\sigma$ configuration with a 90° angle between the incoming and scattered radiation (the π and σ polarization vectors are parallel and perpendicular to the scattering plane, respectively). The polarization of the outgoing X-rays is not measured, so both π and σ are present. This geometry is often used to remove the elastic peak from the RIXS spectra. However, it corresponds to a very particular polarization condition whose effect is often not taken into account. Since the total scattering operator does not include the totally symmetric term a $d_{xy} \rightarrow d_{xy}$ becomes forbidden. However, not only the elastic peak is affected. This becomes clear when comparing the calculations for RIXS in Figs. 1(b) and (c). Note that at the incoming energy indicated by c, we see features A and B for $\sigma \rightarrow \pi\sigma$ and only feature B for $\pi \rightarrow \pi\sigma$. Feature A is a on-rung transition between bonding and antibonding d_{xy} molecular orbitals, which becomes forbidden in a 90° $\pi \rightarrow \pi\sigma$ geometry. The smaller excitation energy of 0.8 eV is in agreement with that found in optical spectroscopy[3]. The energy loss feature at 1.5 eV observed in the geometry used by Zhang *et al.* (indicated by B) corresponds to a local $d_{xy} \rightarrow d_{yz,zx}$ transition.

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[1] G. P. Zhang *et al.*, Phys. Rev. Lett. **88**, 077401 (2002).
[2] H. Smolinski *et al.*, Phys. Rev. Lett. **80**, 5164 (1998)
[3] C. Presura *et al.*, Phys. Rev. B **62**, 16 522 (2000).